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CAPACITOR POWDER

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In order to clarify the two-letter codes and the other abbreviations, refer to the Guidance Notes on Codes and Abbreviations at the beginning of each regular issue of the PCT Gazette.

**(57) Abstract:** The invention relates to an electrolytic capacitor containing a niobium anode, a niobium oxide depletion layer, a semiconducting cathode and an electrolyte, whereby the niobium oxide depletion layer contains at least one metal selected from the group Al, Si, Ti, Zr, Mo, W, Y and Ta.

The present invention is relative to a powder for producing electrolytic capacitors and in particular to a powder for producing anodes for electrolytic capacitors.

The literature describes in particular the acidic-earth metals niobium and tantalum as initial materials for the production of such capacitors. The production of the capacitors takes place by sintering fine powders for producing a large-surface structure, by oxidation of the surface of the sintered body for producing a non-conductive insulating layer and by applying the counterelectrode in the form of a layer of manganese dioxide or of a conductive polymer. The special suitability of the acidic-earth metallic powders is derived from the great relative dielectric constant of the pentoxides.

Up to the present, only tantalum powders had achieved industrial significance for the production of capacitors. This is based on the one hand on the reproducible ability to produce fine tantalum powder and on the other hand on the fact that the insulating oxide layer of tantalum pentoxide has a particularly pronounced stability. This is possibly based on the fact that tantalum, in contrast to niobium, does not form a stable suboxide.

However, the disadvantages of tantalum are becoming increasingly significant as microelectronics development continues. On the one hand, tantalum has a very high density of  $16.6 \text{ g/cm}^3$ . This limits the tendency to reduce weight, in particular the weight of portable electronic devices like mobile telephones, etc. On account of the density of niobium, which is only half as great as that of tantalum, weight-related specific capacities can be achieved that are approximately twice as high as those achieved with tantalum powders, given the prerequisite of the same geometry and the same properties of the oxide layer. The material properties of the insulating pentoxide layer of niobium on the one hand and of tantalum on the other hand that determine the capacity of a capacitor exert partially opposite influences.

Thus, the greater the relative dielectric constant, the higher the capacity of a capacitor. The greater the thickness of the insulating layer required for the particular specified operating voltage, the lower the capacity is. Thus, the higher, at 41, dielectric constant of niobium pentoxide in comparison to 26 of tantalum pentoxide is compensated by the greater thickness of the pentoxide layer required for niobium in comparison to tantalum. At a given anodizing voltage the increase in thickness of the tantalum pentoxide layer is approximately  $2 \text{ nm/V}$  and that of the niobium pentoxide layer is approximately  $3.7 \text{ nm/V}$ . Accordingly, the capacities relative to the surface of the capacitors are comparable.

The use of niobium capacitors was reserved up to the present for low specific capacities with a small specific surface and a rather poor quality.

The present invention has the problem of overcoming the disadvantages of known niobium capacitors. The present invention has the particular problem of improving the niobium pentoxide depletion layer on niobium capacitors in such a manner that greater specific capacities can be realized.

It was found that niobium powders with a surface coating consisting of at least one of the elements Al, Si, Ti, Zr, Mo, W, Y and Ta are superbly suited for the production of niobium capacitors. In particular, it was found that the specific capacity, relative to the surface of the capacitor anode, of such capacitors produced from coated niobium powder is higher than that of pure niobium anodes and that niobium anodes with a low residual current are obtained. Furthermore, first indications exist for a long-time stability comparable to tantalum anodes.

Accordingly, the present invention has as subject matter niobium powder with a surface coating of at least one of the elements Al, Si, Ti, Zr, Mo, W, Y and Ta.

The invention also has as subject matter sintered anodes of niobium for capacitors, which anodes have a surface content of at least one of the elements Al, Si, Ti, Zr, Mo, W, Y and Ta.

Furthermore, the invention also has as subject matter sintered anodes consisting of niobium and provided with a niobium oxide depletion layer that contains at least one of the elements Al, Si, Ti, Zr, Mo, W, Y and Ta.

The invention also has as subject matter electrolytic capacitors consisting of a niobium anode, a niobium oxide depletion layer, a semiconducting cathode and an electrolyte, which niobium oxide depletion layer comprises at least one of the surface-modification elements.

Preferred contents of the surface modification elements in the depletion layer are below 25 atom % relative to the total metal content of the depletion layer and contents up to 20 atom % are especially preferred. Contents of the surface modification element of 2 to 15 atom % in the oxidic depletion layer are further preferred.

The amount of surface coating relative to the niobium powder is preferably less than 18 atom %, in particular less than 15 atom % and more preferably 1.5 to 12 atom %.

Preferred surface modification elements are Ti, Zr and Ta, and Ta is especially preferred.

It is assumed that the surface modification element of the niobium powder remains substantially on the surface even during the further processing to the capacitor since the temperatures of customarily below 1250°C relative to the melting point of niobium of 2500°C and used during the further processing are relatively low for diffusion in solids.

Accordingly, the present invention makes it possible to produce niobium capacitors that exceed the currently available extremely high-capacitive tantalum capacitors. Such tantalum capacitors have specific capacities of 100,000  $\mu\text{FV/g}$  at anodizing voltages of, e.g., 40 V. A niobium capacitor in accordance with the invention with corresponding geometry has specific capacities of above 300,000  $\mu\text{FV/g}$ . In particular, it is possible to produce chemically modified niobium capacitors with a specific capacity, relative to the capacitor surface, of more than 60,000  $\mu\text{FV/m}^2$  and in particular more than 70,000  $\mu\text{FV/m}^2$ .

The invention also has as subject matter a method for producing the capacitor powder of the invention. The method consists in that a niobium powder is impregnated in the solution of a hydrolyzable or decomposable compound of the surface modification element, the powder is separated from the solution, the compound adhering to the powder is hydrolyzed or decomposed, and the hydrolyzate is subsequently reduced to the metal.

Suitable niobium powders are powders obtained by heating niobium metal ingots melted by an electron beam in an atmosphere of hydrogen, grinding the material rendered brittle by the absorption of hydrogen and by removing the hydrogen by heating in a vacuum. Niobium flakes according to WO 98/19811 are also suitable.

In addition, highly-porous niobium powders are suitable that were obtained according to not previously published suggestions of the applicant in accordance with DE 198 31 280, DE 198 47 012 and PCT 99/09772 by reducing niobium pentoxide in liquid or gaseous magnesium, optionally after a preceding reduction to the suboxide by hydrogen.

Furthermore, niobium powders containing one or more of the elements Al, Ti, Mo, W, Hf, Zr or Ta as alloy component, that is, in uniform distribution in amounts up to 5 wt% are suitable as niobium powders.

The application of the surface modification element is described in the following using the example of tantalum.

Potential decomposable and/or hydrolyzable tantalum compounds are in particular organic tantalum compounds soluble in water or in organic solvents. Tantalum oxalate is suitable as a water-soluble organic tantalum compound. Furthermore, alcohol-soluble tantalum alkoxides with 1 to 8 carbon atoms such as tantalum methoxide, tantalum ethoxide, tantalum propoxide, tantalum butoxide, etc. including tantalum octoates are suitable as well as organometallic compounds of tantalum in accordance with US-A 5,914,417.

In order to produce the thin layers of tantalum on the niobium powder the organic tantalum compounds are preferably used in dilute solutions, even to the extent that they are liquid. Water is a suitable solvent in as far as the tantalum compound is stable in water. The alkoxides are preferably used in absolute alcohol or other organic solvents with so little acidity that no hydrolysis takes place without the admission of water, such as toluene or benzene. The particular corresponding alcohol is preferred for the solution of the alkoxides.

The concentration of the tantalum compound in the particular solvent is preferably 1 to 20 wt%, especially preferably 1 to 10 wt% and even more preferably 1 to 5 wt%.

The niobium powder is suspended in the solution of the organic tantalum compound and allowed to stand for a while in order to assure a good wetting. This can typically take 10 minutes to 1 hour. In order to assure a good penetration of porous niobium powder or agglomerates of niobium powder, it can be advantageous to place the niobium powder in a vacuum container under a vacuum, to wash the container with solvent vapors, if necessary, and subsequently to introduce the treatment solution into the evacuated vessel.

The treated niobium powder can be separated from the solution by filtering, centrifuging or decanting.

If tantalum alkoxides are used, they are carefully hydrolyzed in air without the exclusion of moisture or in moistened air, preferably under gentle heating to 50 to 100°C. If necessary, water vapor can be introduced toward the end of the treatment in order to complete the hydrolysis. If tantalum oxalate is used, the hydrolysis is carried out in an aqueous, alkaline

solution, e.g., an ammonia solution or sodium hydroxide solution. The hydrolysis is carried out with particular preference in an ammonia-containing gas flow.

In order to produce a uniformly adhering coating of tantalum oxide the hydrolysis should take place gradually over several hours.

The immersion and hydrolysis can be multiply repeated. It is preferable if the immersion of the niobium powder is carried out in a low concentration solution and carried out multiply.

After a drying step, which is interposed, if necessary, the niobium powder treated in this manner is preferably reduced with a getter metal with a sufficiently high vapor pressure at 850 to 1000°C. Suitable getter metals are magnesium, calcium, strontium, barium, aluminum and/or lanthanum. It is important that the oxides that form during the reduction can be readily washed out with mineral acids. Magnesium is a particularly preferred reduction agent.

The niobium powders that are reduced in this manner, washed with mineral acids and subsequently washed free of acid with demineralized water and dried are pressed in suitable dies up to a pressing density of 2.5 to 3.5 g/cm<sup>3</sup> to pellets and subsequently sintered at 1100 to 1250°C in a known manner. The sintered anodes are contacted with a tantalum wire and/or a niobium wire, preferably by a niobium wire, if the contact wire had not been inserted into the die already during pressing.

Forming is subsequently carried out in a known manner in 0.1 % phosphoric acid up to the desired forming voltage.

In addition to oxalates and alkoxides, aqueous solutions of ammonium paratungstate are suitable and preferred for the production of tungsten coatings, and aqueous solutions of ammonium heptamolybdate that can be thermally decomposed are suitable and preferred for the production of molybdenum coatings.

In order to produce titanium coatings an aqueous solution of  $\text{TiOSO}_4$  is suitable that is hydrolyzed by an aqueous base, e.g., ammonia, or pure  $\text{TiCl}_4$  is suitable that is subsequently hydrolyzed with water vapor.

#### Examples 1 to 7

A high-purity niobium powder is used that was obtained by magnesium vapor reduction of niobium suboxide  $\text{NbO}_2$  according to DE-A 19 831 280. The powder has a specific surface according to BET of 3.02 m<sup>2</sup>/g. Various specimen amounts are immersed in an ethanol solution containing the amounts of tantalum ethoxide indicated in Table 1. A reference specimen is treated in pure ethanol solution. After 30 min the specimen amounts are separated from the particular solution by filtration and allowed to stand 15 min in the ambient air.

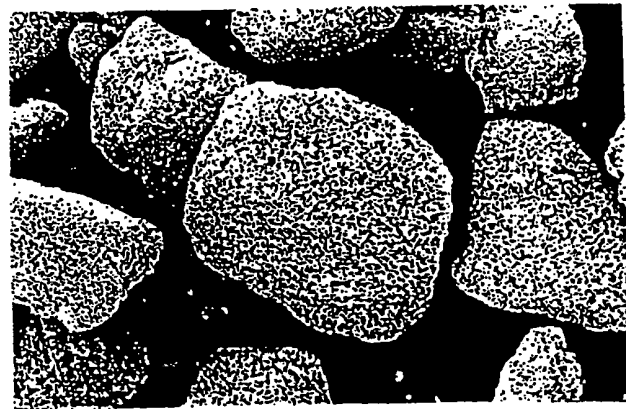
The specimens are subsequently dried for 45 min at 95°C, washed with 80°C demineralized water and re-dried.



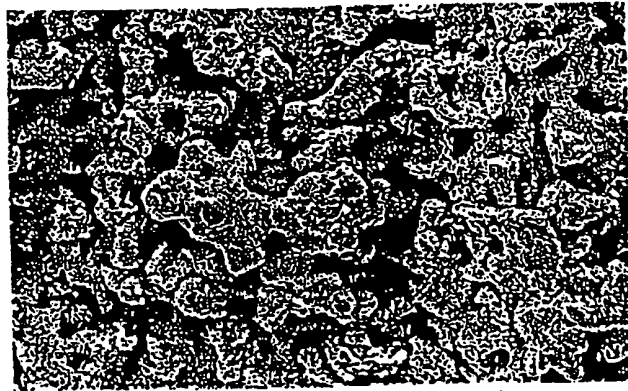


### Claims

1. An electrolytic capacitor containing a niobium anode, a niobium oxide depletion layer, a semiconducting cathode and an electrolyte, which niobium oxide depletion layer contains at least one metal from the group Al, Si, Ti, Zr, Mo, W, Y and Ta.
2. The capacitor according to Claim 1 in which the metal is tantalum.
3. A capacitor anode consisting of sintered niobium powder with a depletion layer produced by anodic oxidation which depletion layer contains at least one of the elements Al, Si, Ti, Zr, Mo, W, Y and/or Ta.
4. A capacitor powder consisting substantially of niobium with a surface coating of at least one of the elements Al, Si, Ti, Zr, Mo, W, Y and/or Ta.
5. A method of producing a capacitor powder according to Claim 4 by immersing an optionally alloyed niobium powder in a solution of a hydrolyzable or decomposable compound of at least one of the elements Al, Si, Ti, Zr, Mo, W, Y and/or Ta, separating the powder from the solution, hydrolyzing or decomposing the adhering compound and if necessary reducing the hydrolyzate to the metal.



00015864 — 100μm HCST



00015865 — 10μm HCST



00015866 — 3μm HCST

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ERSATZBLATT (REGEL 26)

Key: 1 REPLACEMENT PAGE (REGULATION 26)

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 00/10622

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 H0169/042 H0169/052

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 582 844 A (ROEDERSTEIN KONDENSATOREN) 16 February 1994 (1994-02-16) claims 1,3,5,6	1
X	US 3 867 129 A (RONNEAU GERARD S ET AL) 18 February 1975 (1975-02-18) column 1, line 30 - line 40 column 1, line 50 - line 67	4,5
A	US 3 849 124 A (VILLANI G) 19 November 1974 (1974-11-19) column 1, line 11 - column 2, line 6 claim 1	3,4
A	GB 2 106 938 A (STANDARD TELEPHONES CABLES LTD) 20 April 1983 (1983-04-20)	
A	& US 5 914 417 A 22 June 1999 (1999-06-22) cited in the application	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

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\*P\* document published prior to the international filing date but later than the priority date claimed

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\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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## INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/EP 00/10622

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0582844 A	16-02-1994	DE 4225920 A	10-02-1994
US 3867129 A	18-02-1975	NONE	
US 3849124 A	19-11-1974	US 3597664 A	03-08-1971
GB 2106938 A	20-04-1983	NONE	